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Organic Stabilizers for PVC Processing

*Small amounts of monoalkyltin added to stabilizing
compounds can prevent discoloration and degradation
in molded parts*

It is known that halogenated resins and particularly polyvinyl chloride compositions undergo rapid degradation when exposed to heat and air. The result is resin discoloration and deterioration of physical properties. This tendency can usually be reduced significantly, however, by incorporation of various metal-organic or organometallic compounds in resin formulations. Unfortunately, while these metallic stabilizers offer many advantages, ranging from the assurance of long-term stability of a formulation during processing to the impartment of good clarity and physical properties to the finished product, they sometimes also have disadvantages at the concentrations at which they may have to be used. Among the disadvantages are high cost, toxicity, poor early color, or even poor long-term stability.

Using the dehydrochlorination of PVC as an obvious template, most researchers have attempted to explain the role of stabilizers either as hydrogen chloride acceptors or as facile carboxylate-labile chloride exchangers. The latter explanation is widely accepted; indeed model compound and radioisotope studies (1) have shown such exchange to take place. It is reasonable to suppose that a tertiary or allylic chloride has a carbon to chlorine bond distance larger than the oxygen-carbon bond length of the formed tertiary or allylic carboxylic ester. Ostensibly, Group IIB metal soaps exchange rapidly with the labile chlorides in proportion to decreasing atomic number, but they unfortunately give rise to deleterious Lewis acids in the same order. Group IIA metal soaps do not exchange with labile polymer chlorides at nearly equivalent rates, but function by reaction with Group IIB Lewis acids, thereby regenerating the efficacious Group IIB carboxylates. Hence, synergy is conveniently accounted for (2).

Similar thinking has been invoked for organotin stabilizers; however, dibutyltin bis(isooctyl mercaptoacetate) can be recovered almost quantitatively from processed and undegraded PVC, well after unstabilized PVC would have decomposed, but shortly before the onset of rapid hydrogen chloride evolution. This may cast doubt upon the importance of a pro-

posed mechanism of exchange between tertiary chlorides and organotin species (3), but the concentration effect of the stabilizer may be explained away by mass action, and the exchange, as involving very few but very important sites. However, viable mechanistic explanations for vast differences in dynamic stabilization are lacking.

Classical organic stabilizers such as α -phenyl indole, the β -aminocrotonic esters, diphenyltins, and cyano-guanidine have never held much interest, since stabilization efficacy is either in the indifferent neighborhood provided by calcium-zinc soaps or confined to specific interaction cases. Organic auxiliaries used with metal stabilizers are regarded as synergists and not main-effect stabilizers, but most mechanistic thinking is again derived from technical phenomenology, rather than from definitive basic study. Thus phosphites are envisioned as chelators for Lewis acids formed from Group IIB metal carboxylate-chloride exchange; epoxides are hydrogen chloride scavengers; polyols are chelators; and antioxidants primarily stabilize the plasticizer but play a small role to anti-oxidation of the polymer molecule itself. The importance of oxidation in PVC degradation has always been minimized.

In the light of the extrapolative developments of PVC stabilization technology, it seems that past investigators have somewhat neglected the importance of certain elements of the degradation process, particularly oxidation. This is not to say that the influence of oxygen has been ignored (4), but it may well have been somewhat misunderstood (5). It has been recently suggested, however, that the antioxidant role of purely organic materials may play a primary role in the stabilization process of PVC and that metallic species may act as secondary stabilizers (6).

Antioxidants as Stabilizers

In the past, a number of organic compounds containing divalent sulfur have been contemplated as stabilizers against thermal decomposition of PVC (6 and 7). Most of these compounds, such as thiolesulfides, disulfides, polysulfides, thioacetals, and, lately,

Table 1. Comparative thermal stability of flexible PVC formulations stabilized with organic compounds.

No.	Stabilizer structure (2 phr)	Slight (Yellow)	Moderate (Orange)	Substantial (Black)
1	R—S—S—R	10	15	30
2	No. 1 + 5% monoalkyltin	30	50	60
3	R—S—C(R') ₂ —S—R	5	10	20
4	No. 3 + 5% monoalkyltin	40	50	—
5	ROCO(OCH ₂) ₂ —S—S—(CH ₂) ₂ COOR	10	20	40
6	No. 5 + 5% monoalkyltin	40	50	60
7	ROCO(OCH ₂) ₂ —S—C(R') ₂ —S—(CH ₂) ₂ COOR	15	30	45
8	No. 7 + 5% monoalkyltin	50	60	80
9	RCO—S—COR	10	20	40
10	No. 9 + 5% monoalkyltin	50	60	—
11	Barium-cadmium soap	30	50	60

thiolanhydrides, exhibit fair long-term dynamic stabilizing efficacy both for plasticized and rigid PVC formulations, even though they can hardly be considered as effective hydrogen chloride acceptors. Yet they have never gained commercial importance because substantial discoloration of the polymer occurs during processing. Meanwhile, among the numerous types of compounds proposed for the stabilization of PVC, organotin mercaptides and mercaptoesters have been found to be particularly efficient and their commercial use has increased steadily. If the chemical structure of an organotin mercaptide and that of an organic disulfide, for example, were compared, what would they be seen to have in common? Both structures present analogous peroxide decomposing properties which can reasonably be held accountable for the retardation of dehydrochlorination and, perhaps more critically, for the crosslinking of the processed polymer. We say "more critically," because the dynamic processability of a polymer melt is affected less by its loss of hydrogen chloride than by its crosslinking; and the former does not necessarily lead to the latter. What organometallic mercaptides have but organic sulfur compounds have not is a tin atom, whose orbital capacity makes "stabilization" by coordination of chlorine atoms at unstable allylic sites a good probability. Such stabilization would account for only a fraction of the amount of organotin stabilizer normally used in PVC formulations, but if consideration is given to the fact that dibutyltin bis(2-octylmercaptacetate) can be recovered almost quantitatively from processed undegraded PVC well before the extensive evolution of hydrogen chloride, it is tempting to find stabilization by coordination more attractive than stabilization by exchange reactions.

Actually, the disadvantages of organic divalent sulfur compounds can be overcome by the inclusion of small amounts of monohydrocarbyltin compounds with organic thio compounds (8 and 9). Evidently, the stabilizing efficacy of such mixed stabilizers is directly influenced by the structure of the organic primary stabilizer acting as a peroxide decomposer or peroxide trap. Among the more effective species are

the mercaptoles and mercaptals of mercaptopropionic acid esters, long-chain alkyl thiolanhydrides and disulfides, as well as certain acyl mercaptoles. Structure elaboration can also optimize the activity of the organotin synergist, although only to a certain extent. In all cases, the incorporation of a well-balanced lubricating system is naturally of considerable help.

Experimental Procedure

Twelve formulations were prepared, each containing 100 parts of a general-purpose polyvinyl chloride suspension resin, 25 parts of dioctyl phthalate, 0.5 parts of two parts of the respective stabilizers indicated in Table 1. Each formulation was processed on a two-roll mill at 320°F for 5 min. Samples of each formulation were baked in an air circulatory oven at 370°F and removed periodically. The general structure of the stabilizers are given in Table 1. Slight discoloration represents the time for some yellowing of the test sample to occur; moderate discoloration represents the time for an orange or red discoloration to occur. Rigid formulations, similar to those described, but from which the plasticizer had been deleted, were processed in a torque rheometer at 200°C and 50 rpm for 60g charge. The experimental results are summarized in Table 2.

The activity of a monoalkyltin co-stabilizer, which depends upon the structure of the compounds, may be divided into two areas, according to the general effect each has on the formulation. The first is truly synergistic inasmuch as very often the monoalkyltin compound is not a stabilizer by itself, regardless of the amount used, although it exhibits a maximum activity at a specific usage level, as indicated in Table 3. However, the second is dynamically additive when the monoalkyltin compound can be used by itself as a primary stabilizer. This can best be illustrated by a statistical analysis of organic stabilizer/tin synergist performance on a torque rheometer.

Thiobaclic anhydride (TLA) was the organic compound of choice for this experiment, since it has

Table 2. Dynamic stability of rigid PVC formulations.

No.	Stabilizer structure (2 phr)	Stability time, min	Minimum torque, meter-grams
1	$\text{ROCO}(\text{CH}_3)_2-\text{S}-\text{C}(\text{R})_2-\text{S}-\text{C}(\text{H}_3)_2\text{COOR}$	6.9	1860
2	No. 1 + 5% monoalkyltin	7.1	1660
3	Di-n-butyltin bis(isooctylmercaptoacetate)	7.6	1790

Table 3. Effect of organotin co-stabilizer on the efficacy of an organic stabilizer.

Amount of monoalkyltin, phr	Time to slight discoloration, min
0	0
0.005	20
0.1	30
0.15	20
1.0	5

Table 4. Thioleauric anhydride dynamic stabilization.*

TLA, % on PVC	Synergist % on PVC	Stability time, min		Minimum torque, meter-grams	
		190°C	200°C	190°C	200°C
3.0	0.45	8.5	7.5	1900	1775
3.0	0.15	7.5	6.6	2000	1800
1.0	0.15	6.2	4.5	2100	2150
1.0	0.05	5.5	—	2300	—
2.0	0.20	6.8	6.1	2000	1850
2.0	0.40	7.1	6.3	2010	1925
4.0	0.40	8.9	8.0	1900	1650
2.0	0	6.7	5.7	2010	1850
0	0	3.4	3.4	2850	2850

* Brabender Plastograph, 50 rpm, 60 g charge.

tions as quite an efficacious primary stabilizer for plasticized PVC (7). It gave excellent dynamic stabilization of rigid PVC, but immediate and uniform amber discoloration would occur during plastication unless a monoalkyltin compound were used as a co-stabilizer.

The experimental array of TLA/synergist combinations was laid out in a simple composite star design. All compounds were Henschel blended and processed to degradation on a Brabender Plastograph at a shear rate of 50 rpm and at temperatures of 190 and 200°C. A typical response curve is illustrated in Fig. 1, and the results are given in Table 4. Regressive analysis yielded polynomial curves in quite good agreement with the actual data. Anticipated curvature due to stabilization loss at higher concentrations is either insignificant or lost for the synergist. Figure 2 shows fitted response curves for both temperatures between 0-20% synergist based on TLA content. As a control, analogous PVC (plus 0.75% of ester lubricant) stabilized with 1, 2, and 3% dibutyltin bis(isooctylmercaptoacetate), or DBT(IOTG), was sheared at the two temperatures. Resultant data is given in Table 5. Since there was no apparent indication of negative curvature over this concentration range, the data were least square fitted to the graph of Fig. 3, which shows that the organotin stabilizer is at least more efficacious than TLA, with or without synergist, on an equivalent concentration basis. However, on an equivalent metal basis (Table 6) something new emerges. DBT(IOTG), contains 17% tin, while the TLA package has at most 20% of a 10% tin containing component. Thus, only a small fraction of the metal is required to accomplish the same stabilization afforded by 1.0-1.5 parts of the commodity organotin sta-

Table 5. Dibutyltin bis(isooctylmercaptoacetate) dynamic stabilization.*

DBT(IOTG), % on PVC	Stability time, min		Minimum torque, meter-grams	
	190°C	200°C	190°C	200°C
1.0	6.6	6.0	1990	1850
2.0	11.3	9.1	1775	1600
3.0	17.4	16.0	1710	1550

* Brabender Plastograph, 50 rpm, 60 g charge.

Table 6. Equivalents in dynamic stabilization efficacy for dibutyltin mercaptide and thioleauric anhydride.

Temper- ature, °C	DBT(IOTG), mg Sn/100 g PVC	TLA + 20% Syn = mg Sn/100 g PVC	TLA alone
190	1.0	180	1.63
200	1.0	180	1.80
190	1.5	270	3.3
200	1.5	270	3.0
			66
			—
			60
			3.7

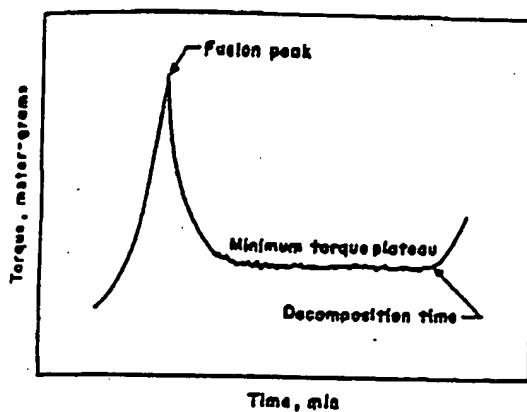


Figure 1. Typical Brabender plastograph curve.

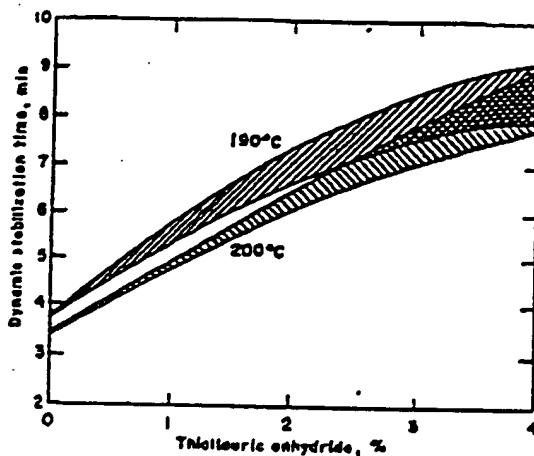


Figure 2. Effect of TLA on dynamic stabilization time (variance 0.20% synergist on TLA).

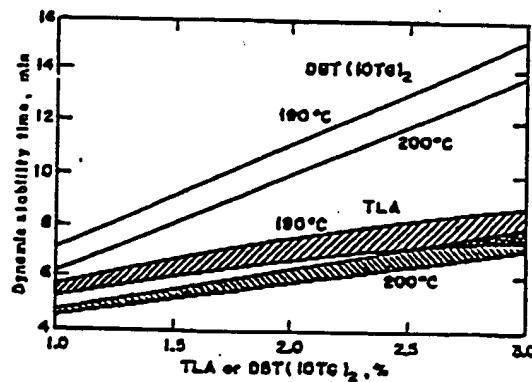


Figure 3. Comparison of stabilization efficacies: thiolauric anhydride vs dibutyltin bis(isooctylmercaptoacetate).

Table 7. Comparative "per tin" dynamic stabilization efficacy of synergist and dibutyltin mercaptide.

Stabilizer	Plastograph stability, min/g tin metal	
	190°C	200°C
DBT(IOTC) L₂	23.2	20.9
Synergist (mg/10.0 g PVC)		
2	26.5	
4	20.8	11.3
6	17.7	13.3
8	17.9	14.4
Average	20.7	13.0

bilizer. Stabilization provided by higher DBT(IOTC) levels is apparently not reached by practical levels of the TLA system, a condition that may be less important today than previously. Twin-screw extrusion, for example, is commercially successful at DBT(IOTC) levels as low as 0.6%.

The question remains: Is the monoalkyltin compound a true synergist with respect to dynamic stabilization? Table 7 would indicate otherwise, for the magnitude of the additive effect of this synergist (on top of TLA) is relatively constant and certainly equivalent to or less than that of DBT(IOTC). The synergistic effect ascribed to this monoalkyltin compound lies in its ability to inhibit the amber discoloration that seems to accompany TLA stabilization of unplasticized PVC. It is important to realize that the normal process for stabilizer screening starts with such static (oven bake) testing, and that initial observations on the behavior of "unsynergized" TLA would most probably have precluded further experimentation. It should also be noted that the synergy observed between the monoalkyltin compound and the thiolanhydride is not confined to TLA, but is found with the whole class of sulfur-containing antioxidants (6). Finally, melt viscosities generated by organic stabilizer systems are comparable to those of DBT(IOTC), at equivalent stabilization (lower levels), and this is important in commercial rigid PVC processing. The upward inflection of the TLA systems shown at high levels (Fig. 4) may be due to experimental inaccuracy or may actually reflect interchain bonding by the increasing content of monoalkyltin compound.

Conclusion

The overall stabilizing efficacy of traditional organotin mercaptides cannot yet be surpassed when the latter are used in relatively high concentrations (e.g., 2.0 phr). But at lower usage levels, the performance comparison, when based on tin concentration, speaks highly in favor of the new organic systems. Considering the present trend to process PVC formulations on equipment requiring much lower levels of stabilizer

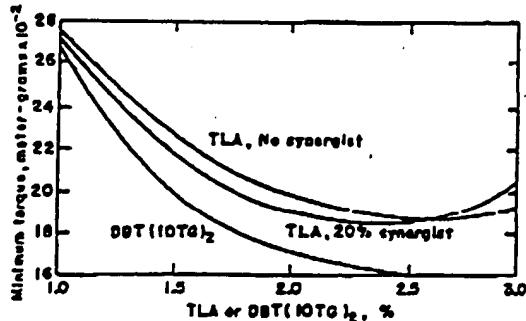


Figure 4. Effect of thioauric anhydride or dibutyltin bis(isooctylmercaptoacetate) on processing torque at 190°C.

(on twin-screw extruders), the prospects of organic primary stabilizers both in rigid and plasticized applications are very good indeed. Proprietary mercaptolates or thiolanhydrides in combination with small amounts of monalkyltin synergists are seen out-performing calcium-zinc systems and approaching the

effectiveness of organotin stabilizers. Consequently, inexpensive extrudates and blow-molded containers exhibiting excellent color can now be obtained in the plant. Considerable care must still be given to the formulation of PVC blends stabilized with organic thio compounds, especially lubrication, and it was found that these primary stabilizers can easily accommodate other organic co-stabilizers such as phosphites and epoxides. Phenolic antioxidants can be incorporated usefully into formulations, either as an intimate part of the chemical structure of the thio compound or as a separately blended entity. As in cases of oxidative degradation of various other polymers, hindered phenols may act synergistically with sulfur-containing peroxide decomposers to reduce degradation of polyvinyl halides. A multitude of possibilities thus appear to be available to the processor for the future production of a wide variety of rigid as well as flexible PVC moldings, at a substantially lower cost.

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